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PATENT

UNITED STATES PATENT APPLICATION
of
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for
SYSTEM AND METHOD FOR HYDROTHERMAL
REACTIONS – TWO LAYER LINER

FIELD OF THE INVENTION

The present invention pertains generally to methods and systems for hydrothermal treatment to destruct waste, recovery heat, or produce beneficial chemicals. More specifically, the present invention pertains to methods and systems for the hydrothermal treatment of organics which contain inorganic compounds such as salts or oxides or which will generate these inorganic compounds. The present invention is particularly, but not exclusively, useful as a method and system for the hydrothermal treatment of organics under supercritical temperature and pressure conditions, or at supercritical temperatures and elevated, yet subcritical pressures.

BACKGROUND OF THE INVENTION

The process of wet oxidation has been used for the treatment of aqueous streams for over thirty (30) years. In general, a wet oxidation process involves the addition of an oxidizing agent, typically air or oxygen, to an aqueous stream at elevated temperatures and pressures. The resultant "combustion" of organic or inorganic oxidizable materials occurs directly within the aqueous phase.

A wet oxidation process is typically characterized by operating pressures in the range of 30 bar to 250 bar (440 psia-3,630 psia) and operating temperatures in a range of one hundred fifty degrees Celsius to three hundred seventy degrees Celsius (150°C-370°C). Under these conditions, liquid and gas phases coexist for aqueous media. Since gas phase oxidation is quite slow at these temperatures, the reaction is primarily carried out in the liquid phase. To do this, the reactor operating pressure is typically maintained at or above the saturated water vapor pressure. This causes at least part of the water to be present in a liquid form. Even in the liquid phase, however, reaction times for substantial oxidation are on the

order of one (1) hour. In many applications, reaction times of this length are unacceptable.

In addition to unacceptably long reaction times, the utility of conventional wet oxidation is limited by several factors. These include: the degree of oxidation attainable; an inability to adequately oxidize refractory compounds; and the lack of usefulness for power recovery due to the low temperature of the process. For these reasons, there has been considerable interest in extending wet oxidation to higher temperatures and pressures. For example, U.S. Pat. No. 2,944,396, which issued July 12, 1960 to Barton et al., discloses a process wherein an additional second oxidation stage is accomplished after wet oxidation. In the Barton process, unoxidized volatile combustibles which accumulate in the vapor phase of the first stage wet oxidation reactor are sent to complete their oxidation in the second stage. This second stage is operated at temperatures above the critical temperature of water, about three hundred seventy four degrees Celsius (374°C).

A significant development in the field occurred with the issuance of U.S. Pat. No. 4,338,199, to Modell on July 6, 1982. Specifically, the Modell '199 patent discloses a wet oxidation process which has now come to be widely known as supercritical water oxidation ("SCWO"). As the acronym SCWO implies, in some implementations of the SCWO process, oxidation occurs essentially entirely at conditions which are supercritical in both temperature (>374°C) and pressure (>about 3,200 psi or 220 bar). Importantly, SCWO has been shown to give rapid and complete oxidation of virtually any organic compound in a matter of seconds at temperatures between five hundred degrees and six hundred fifty degrees Celsius (500°C-650°C) and at pressures around 250 bar. During this oxidation, carbon and hydrogen in the oxidized material form the conventional combustion products, namely carbon dioxide ("CO₂") and water. When chlorinated hydrocarbons are involved, however, they give rise to hydrochloric acid ("HCl"), which will react with available cations to form chloride salts. Due to the corrosive effect of HCl, it may be necessary to intentionally add alkali to the reactor to avoid high concentrations of hydrochloric acid in the reactor. This is especially

important in the cooldown equipment following the reactor. In a different reaction, when sulfur oxidation is involved, the final product in SCWO is a sulfate anion. This is in contrast to standard, dry combustion, in which gaseous sulfur dioxide ("SO₂") is formed and must generally be treated before released into the atmosphere. As in the case of chloride, alkali may be intentionally added to avoid high concentrations of corrosive sulfuric acid. Similarly, the product of phosphorus oxidation is a phosphate anion.

At typical SCWO reactor conditions, densities are around 0.1 g/cc. Thus, water molecules are considerably farther apart than they are in water at standard temperatures and pressures (STP). Also, hydrogen bonding, a short-range phenomenon, is almost entirely disrupted, and the water molecules lose the ordering that is responsible for many of the characteristic properties of water at STP. In particular, the solubility behavior of water under SCWO conditions is closer to that of high pressure steam than to water at STP. Further, at typical SCWO conditions, smaller polar and nonpolar organic compounds, having relatively high volatility, will exist as vapors and are completely miscible with supercritical water. It also happens that gasses such as nitrogen (N₂) oxygen (O₂) and carbon dioxide (CO₂) show similar complete miscibility in supercritical water. The loss of bulk polarity in supercritical water also significantly decreases the solubility of salts. The lack of solubility of salts in supercritical water causes the salts to precipitate as solids and deposit on process surfaces causing fouling of heat transfer surfaces and blockage of the process flow.

A process related to SCWO known as supercritical temperature water oxidation ("STWO") can provide similar oxidation effectiveness for certain feedstocks but at lower pressure. This process has been described in U.S. Patent No. 5,106,513, issued April 21, 1992 to Hong, and utilizes temperatures in the range of six hundred degrees Celsius (600°C) and pressures between 25 bar to 220 bar. On the other hand, for the treatment of some feedstocks, the combination of temperatures in the range of four hundred degrees Celsius to five hundred degrees Celsius (400°C-500°C) and pressures of up to 1,000 bar (15,000 psi) have proven useful to keep certain

inorganic materials from precipitating out of solution (Buelow, S.J., "Reduction of Nitrate Salts Under Hydrothermal Conditions," Proceedings of the 12th International Conference on the Properties of Water and Steam, ASME, Orlando, Florida, September, 1994).

5 The various processes for oxidation in an aqueous matrix (e.g. SCWO and STWO) are referred to collectively as hydrothermal oxidation, if carried out at temperatures between about three hundred seventy-four degrees Celsius to eight hundred degrees Celsius (374°C-800°C), and pressures between about 25 bar to 1,000 bar. Similar considerations of reaction rate,
10 solids handling, and corrosion also apply to the related process of hydrothermal reforming, in which an oxidant is largely or entirely excluded from the system in order to form products which are not fully oxidized. The processes of hydrothermal oxidation and hydrothermal reforming will hereinafter be jointly referred to as "hydrothermal treatment."

15 A key issue pertaining to hydrothermal treatment processes is the means by which feed streams containing or generating sticky solids are handled. It is well-known that such feed streams can result in the accumulation of solids that will eventually plug the process equipment. Sticky solids are generally comprised of salts, such as halides, sulfates, carbonates,
20 and phosphates. One of the earliest designs for handling such solids on a continuous basis is disclosed in U.S. Pat. No. 4,822,497. In general, and in line with the disclosure of the '457 patent, the reaction is a hydrothermal treatment process carried out in a vertically oriented vessel reactor. Solids form in the reactor as the reaction proceeds and these solids are projected to
25 fall into a cooler brine zone that is maintained at the bottom of the reactor. In the brine zone, the sticky solids re-dissolve and may be continually drawn off in the brine from the reactor. Solids separation from the process stream is achieved because only the fraction of the process stream that is necessary for solids dissolution and transport is withdrawn as brine. The balance of the
30 process stream, which is frequently the largest portion, is caused to reverse flow in an upward direction within the reactor. The process stream, less the solids, is then withdrawn from the top section of the reactor. By this means, it

becomes possible to recover a hot, nearly solids-free stream from the process. To minimize entrainment of solid particles in the upward flow within the reactor, the velocity is kept to a low value by using a large cross-section reactor vessel. Experience has shown that while a large fraction of the sticky
5 solids is transferred into the brine zone, a certain portion also adheres to the vessel walls, eventually necessitating an online or off-line cleaning procedure.

The extreme temperatures, pressures, corrosives and insoluble salts present in the hydrothermal reactor vessel present what can only be characterized as a harsh environment to the pressure bearing wall of the
10 reactor vessel. To alleviate the effects of this environment on the pressure bearing wall, liners have been heretofore suggested to separate the reactor chamber from the pressure bearing wall. For example, U.S. Patent No. 5,591,415 which issued to Dassel et al. entitled "Reactor for Supercritical Water Oxidation of Waste" discloses a reactor enclosed in a pressure vessel
15 in a manner that the walls of the pressure vessel are thermally insulated and chemically isolated from the harsh environment of the reaction zone. Unfortunately, the liner disclosed by Dassel et al. fails to adequately address the problem associated with insoluble salt buildup and reactor plugging. Similarly, U.S. Patent No. 3,472,632 which issued on October 14, 1969 to
20 Hervert et al. entitled "Internally Lined Reactor for High Temperatures and Pressures and Leakage Monitoring Means Therefore" discloses a liner that is not sealed to the vessel wall and that has a porous layer for a high temperature reactor. Hervert et al., however, does not disclose the use of the liner for hydrothermal treatment environments, and consequently, the
25 disclosed liner lacks at least one very important feature necessary for using a liner in hydrothermal treatment, namely, a suitable mechanism for relieving the effects of insoluble salt buildup and reactor plugging.

In light of the above, it is an object of the present invention to provide a liner to protect the pressure bearing wall of a hydrothermal treatment reactor
30 incorporating a mechanism to control the liner temperature and thereby prevent the buildup of insoluble salts on the liner. Another object of the present invention is to provide a liner to protect the pressure bearing wall of a

hydrothermal treatment reactor wherein the liner incorporates a mechanism for pre-heating the reaction chamber before steady state treatment conditions are achieved. Yet another object of the present invention is to provide a liner to protect the pressure bearing wall of a hydrothermal treatment reactor wherein the liner incorporates a mechanism for passing a heat exchange fluid by the reactor chamber to allow heat to be recovered from the reaction. Still another object of the present invention is to provide a liner to protect the pressure bearing wall of a hydrothermal treatment reactor wherein the liner incorporates a mechanism for altering the liner temperature, and consequently the liner dimensions, to allow for easy installation and removal of the liner. Still another object of the present invention is to provide a liner to protect the pressure bearing wall of a hydrothermal treatment reactor wherein the liner includes a system for leak detection that is operable during the hydrothermal reaction which allows for reactor shutdown before a severe attack on the pressure bearing wall occurs. Yet another object of the present invention is to provide a system and method for accomplishing hydrothermal treatment which is easy to implement, simple to use, and cost effective.

SUMMARY OF THE PREFERRED EMBODIMENTS

In accordance with the present invention, a system for performing hydrothermal treatment at temperatures above three hundred seventy-four degrees Celsius (374°C) and pressures above about 25 bars, includes a reactor vessel that is formed with a pressure bearing wall which surrounds a reactor chamber. Generally, the feed material is introduced into the reactor chamber from one end of the reactor vessel and the reaction products are withdrawn from the other end of the reactor vessel.

The surface of the pressure bearing wall that faces the reactor chamber is covered by a liner to protect the wall from exposure to temperature extremes, corrosives and salt deposits. The liner is formed with a porous layer and a non-porous, corrosion resistant layer. The corrosion

resistant layer is positioned adjacent to the porous layer to interpose the porous layer between the corrosion resistant layer and the wall of the vessel. Seals extend from the ends of the corrosion resistant layer to the wall of the reactor vessel to further encapsulate the porous layer between the wall and the corrosion resistant layer.

A connector extending through the pressure bearing wall of the reactor vessel is provided to allow fluid communication between the porous layer and an externally located pump. When activated, the pump allows a heat transfer fluid to be pumped into the porous layer for circulation within the porous layer.

10 A second connector in the wall provides an exit for heat transfer fluid circulating within the porous layer. The discharged heat transfer fluid that is flowing through the second connector can be piped back to the pump or to a storage reservoir for recirculation.

In addition to the connectors used for pumping of the heat transfer fluid, one of the heat transfer fluid connectors , or another connector may be provided in the wall of the reactor vessel to allow for sampling of the fluid within the porous layer. Specifically, the purpose of this sampling will be to determine whether a leak has developed in the corrosive layer of the liner. To do this, the physical or chemical properties of a sample may be measured by a sensor. Physical and chemical properties that may be useful for this purpose include: fluid pressure; fluid flow; fluid temperature; and detection of the presence of a particular chemical species in the fluid. For the present invention, the leak detection connector can function in at least two different ways. In one configuration, a sensor can be positioned within the porous layer allowing the connector to function as a conduit to relay a signal from the sensor to a recorder / display. Alternatively, the connector can function as a fluid passageway allowing the fluid from the porous layer to flow through the connector to an externally located sensor. In either case, the connectors allow for leak detection measurements to be performed during the hydrothermal treatment of the reactants thereby ensuring the continuous integrity of the corrosion resistant layer of the liner.

For the present invention, partitions can be positioned within the porous layer, with each partition extending from the corrosion resistant layer to the pressure bearing wall. Thus, the partitions divide the porous layer into sections and isolate the sections from each other. If partitions are used,
5 separate connectors can be provided for each section to thereby allow each section to be independently heated, cooled and monitored for leaks. Also, an optional layer of insulation can be selectively interposed between the porous layer of the liner and the wall of the reactor vessel to insulate the pressure bearing wall of the reactor vessel.

10 In operation, a warming fluid can be selectively passed through the porous layer to pre-heat the reactor chamber during periods preceding steady state treatment conditions. Additionally, a coolant can be selectively passed through the porous layer of the liner during the hydrothermal treatment of the reactants to cool the pressure bearing wall and the corrosion resistant layer of
15 the liner. By maintaining the temperature of the corrosion resistant layer of the liner at sub-critical temperatures, corrosion rates can be reduced and the accumulation of insoluble salts on the liner can be prevented. Also in accordance with the present invention, the connectors can be utilized to perform leak detection measurements during the hydrothermal treatment of
20 the reactants to ensure the continuous integrity of the corrosion resistant layer of the liner.

BRIEF DESCRIPTION OF THE DRAWINGS

The novel features of this invention, as well as the invention itself, both as to its structure and its operation, will be best understood from the
25 accompanying drawings, taken in conjunction with the accompanying description, in which similar reference characters refer to similar parts, and in which:

Figure 1 is a schematic diagram of the components of a system in accordance with the present invention;

Figure 2 is a schematic cross-sectional representation of an exemplary downflow reactor including a two layer liner in accordance with the present invention; and

Figure 3 is a schematic cross-sectional representation for an embodiment of the present invention having a layer of insulation positioned between the reactor vessel wall and the two layer liner.

DESCRIPTION OF THE PREFERRED EMBODIMENT

Referring initially to Figure 1, a hydrothermal treatment system in accordance with the present invention is shown schematically and is generally designated 10. As shown, the system 10 includes a reactor vessel 12 formed with a pressure bearing wall 15 that surrounds a reactor chamber 14. It is also shown that the reactor vessel 12 has an end 16 and an end 18. It is to be appreciated that the vessel 12 can be oriented vertically, horizontally or at an orientation somewhere therebetween.

The feed material to reactor vessel 12 of the system 10 can, in certain embodiments, include several separate identifiable constituents. These are: (i) the reactant to be processed; (ii) an auxiliary fuel, if necessary to sustain reaction in the reactor chamber 14; (iii) water; and (iv) oxidizer(s). More specifically, Figure 1 shows that the reactant 20 which is to be processed is initially held in a holding tank 22. As contemplated for the present invention, the reactant 20 can consist of organic material, inorganics, sludge, soil, neutralizing agents, salt-forming agents, minerals, and/or combustible material. Further, particulates capable of entering and exiting the reactor vessel 12 can be added to the reactant 20 to remove salt from the reactor vessel 12. These particulates can be inert materials such as sand, silica, soil, titanium dioxide, clay, metal, or ceramic. Also, catalyzing materials such as zeolites, heavy metal oxides or noble metals may be used. In either case, the particulates can be added to the reactor vessel 12 to thereby allow insoluble salts to adhere to the surface of the particulate. The coated particulate may

then be removed from the reactor vessel 12. As indicated in Figure 1, it may be necessary to combine this reactant 20 with an auxiliary fuel 24, such as ethanol, which can be initially held in a holding tank 26.

Figure 1 shows that both the reactant 20 and the auxiliary fuel 24, if used, are pressurized before being introduced into the reactor chamber 14. Specifically, a transfer pump 28 and high pressure pump 30 are used to pressurize the reactant 20. Similarly, a transfer pump 32 and a high pressure pump 34 are used to pressurize the auxiliary fuel 24. As shown in the schematic of system 10 in Figure 1, the pressurized reactant 20 and auxiliary fuel 24 are combined in line 36 and transferred to the end 16 of the reactor vessel 12. It is to be noted that while the reactant 20 and auxiliary fuel 24 are respectively pressurized by high pressure pumps 30 and 34 to pressures above about 25 bar, they are not necessarily raised in temperature prior to being introduced into the reactor chamber 14. Thus, as intended for the system 10, the reactant 20 can be introduced into the reactor chamber 14 at ambient temperatures.

In addition to the reactant 20 and auxiliary fuel 24, the feed material to reactor chamber 14 can also include pressurized water 38 and a pressurized oxidizer 39. Specifically, water 38 is drawn from holding tank 40 by transfer pump 42 and is thereafter pressurized by high pressure pump 44 before it is passed into line 46. At the same time, oxidizer 39, is drawn from holding tank 41 and pressurized by a compressor 48 and is passed into the line 46. For purposes of the present invention, the oxidizer 39 to be used, as an alternative to air, can be pure liquid or gaseous oxygen, enriched air, hydrogen peroxide, nitric acid, nitrous acid, nitrate, and nitrite. Alternatively, a substoichiometric amount of oxidizer 39 can be used for applications in which partial oxidation of the reactant 20 is desired. In any event, at this point the pressurized water 38 and compressed air (oxidizer 39) are mixed and introduced into a preheater 50. As contemplated by the present invention, the heating of the pressurized water/air mixture in preheater 50 can be accomplished in several ways. For example, this preheat may be accomplished by a regenerative heat exchange with a hot reaction stream

from reactor chamber 14. The preheat can also be accomplished by an external source, such as electricity, or a fired heater, or a combination of these. External heat sources must be used for preheater 50 when a cold startup of the system 10 is required. On the other hand, it should also be
5 noted that for reactant 20 which has sufficient inherent heating value by itself, the preheater 50 may be shut down once a steady state operation of the system 10 has been achieved.

As the air/water mixture leaves the preheater 50, it is mixed with the reactant 20 and auxiliary fuel 24 from the line 36. This mixing occurs at the
10 junction 52, and the feed material, including the combination of reactant 20, auxiliary fuel 24, water 38, and compressed air (oxidizer 39) is then introduced into the reactor chamber 14 via a duct 54. As will be appreciated by the skilled artisan, an alternative for the system 10 is to use separate ducts for introducing one or more of the streams which make up the feed material
15 into the reactor chamber 14. If so, one duct could be used for the introduction of the reactant 20 and auxiliary fuel 24, and another duct would be used for the introduction of water 38 and an oxidizer 39. Similarly, a separate duct could be used for the reactant 20, the auxiliary fuel 24, the water 38, and the oxidizer 39. Further, depending upon the particular reactant 20, it may be
20 important to use a high shear mixer (not shown) at the junction 52 to mix the feed/fuel stream from line 36 with the water/oxidizer stream from the preheater 50. For example, if the reactant 20 is largely water insoluble, high shear mixing is desirable to ensure sufficient mixing of combustible materials and high pressure oxidizer 39.

25 Referring now to Figure 2, a representative vessel 12 incorporating the features of the present invention is shown. Specifically, the vessel 12 shown in Figure 2 is representative of a downflow reactor as disclosed in U.S. Patent No. 6,054,057 entitled "Downflow Hydrothermal Treatment" which issued to Hazlebeck and is assigned to the same assignee as the present invention. It
30 is to be appreciated that other reactor vessel configurations known in the pertinent art, such as a reversible reactor, can be used with the present invention. As shown in Figure 2, the vessel 12 generally defines a

longitudinal axis 56 and is formed with a wall 15. For the case of a downflow vessel, the longitudinal axis 56 of vessel 12 is vertically oriented with the end 16 directly above the end 18. With this orientation, all of the material that is to be introduced into the reactor chamber 14 through the duct 54 is passed through a nozzle 58. For the exemplary downflow vessel, the nozzle 58 introduces a stream of material 60 into the reactor chamber 14 of the vessel 12 in a direction which is substantially along the axis 56. The nozzle 58 can introduce a straight single jet of the stream 60 or the nozzle 58 can consist of a plurality of nozzles 58 with their respective streams 60 introduced as jets which are inclined toward the axis 56. With this inclination, the streams 60 are directed slightly toward each other for collision with each other.

For the representative downflow reactor vessel, the reaction stream 60 is introduced into the upper portion of the reactor chamber 14 where it is subjected to vigorous back-mixing. Specifically, fluid flow in this back-mixing section 62 is characterized by a turbulence in the reaction stream 60 that results from entraining shear forces and eddies 64 which are set up as the feed material enters into the reactor chamber 14. The feed material is thus rapidly brought above the supercritical temperature of three hundred seventy-four degrees Celsius (374°C) and rapid reaction commences.

For the representative downflow vessel 12 shown in Figure 2, a plug flow section 66 is located below a back-mixing section 62 in reactor chamber 14. This plug flow section 66 is characterized by the fact that there is no large scale back-mixing of the reaction stream 60 in this lower portion of the reactor chamber 14. The flow of the reaction stream 60 in the plug flow section 66, however, does exhibit local turbulent mixing. In certain applications, it may be advantageous to provide a filtering device (not shown) below the plug flow section 66. Such a device is useful for trapping low levels of sticky solids or for retaining particulates within the reactor until they have been completely reacted.

The representative downflow vessel 12 can also include a quenching section 67 as shown in Figure 2 to cool the effluent stream. It may be

desirable to quench the effluent stream for a number of reasons, including to re-dissolve any solids that may have developed during the reaction and/or to adjust the pH of the effluent stream. Returning to Figure 1, for the moment, it can be seen that a high pressure pump 68 is positioned to take water 38 from holding tank 40 and pass it along via line 70 to an input duct 72 (See Figure 2) near the end 18 of the reactor chamber 14. The water 38 injected through duct 72 is used for quenching the reaction stream 60 in the quenching section 67. Specifically, the quenching fluid that is introduced through duct 72 mixes with the reaction stream 60 and re-dissolves any sticky solids which developed during reaction in the reactor chamber 14. This quenching occurs below the quench fluid level 74, but above the exit port 76, so that the reaction stream 60 can pass through exit port 76 and into the line 77 without causing plugging or fouling of the exit port 76.

It will be appreciated by the skilled artisan that fluids such as high pressure gas, rather than water, can be used as a quenching medium. Also, it will be appreciated that water from an external source, or relatively dirty water (e.g., sea water), or cool, recycled reaction stream 60 can be used as a quenching medium. These options would help to reduce the amount of clean quench water needed by the system 10. Additionally, it should be appreciated that the quenching fluid be maintained at temperatures low enough to allow salts to dissolve in the quenching fluid.

Importantly, as seen in Figure 2, a liner 82 is disposed within the reactor chamber 14, covering a portion of the inner surface 84 of the vessel 12. As shown, the liner includes a porous layer 86 and a non-porous, corrosion resistant layer 88. For the present invention, the corrosion resistant layer 88 is positioned adjacent to the porous layer 86 to interpose the porous layer 86 between the corrosion resistant layer 88 and the inner surface 84 of the vessel 12. As such, the corrosion resistant layer 88 is positioned for contact with the reactants 20 in the reactor chamber 14. For purposes of the present invention, the corrosion resistant layer 88 can be made from suitable corrosion resistant materials known in the pertinent art including titanium, platinum, iridium, titania, and zirconia. The corrosion resistant layer 88 is

preferably solid or of a suitable construction to prevent fluid from passing from the reactor chamber 14 to the porous layer 86. For this purpose, seals 90 are located at the ends 92, 94 of the porous layer 86, to attach the corrosion resistant layer 88 to the vessel 12 to thereby encapsulate the porous layer 86
5 between the corrosion resistant layer 88 and the inner surface 84 of the vessel 12.

The porous layer 86 can be a powder such as a metallic powder (sintered or unsintered), a metal or other suitable material having machined pores, a porous ceramic (sintered or unsintered), an expanded metal or
10 metallic foam, or any other material known in the pertinent art that is sufficiently porous to allow fluid to flow through the porous layer 86. Further, for purposes of the present invention, the porosity of the porous layer 86 can be substantially uniform or a porosity gradient may be established in the porous layer 86 to selectively channel fluid flow. In the preferred embodiment
15 of the present invention, the porous layer 86 does not need to be pressurized, and consequently, the liner 82 is capable of transmitting the pressure generated in the reactor chamber 14 from the reactor chamber 14 to the walls 15 of the vessel 12. Alternatively, the porous layer 86 can be pressurized during operation to levels that are equal or greater than the pressures
20 experienced in the reactor chamber 14, thereby allowing the use of liner materials that would be otherwise incapable of transmitting the pressure from the reactor chamber 14 to the wall 15 of the reactor vessel 12 without collapsing.

As will be appreciated from the detailed discussion below, in
25 accordance with the present invention, the porous layer 86 can be used to perform several functions including: detecting leaks in the corrosion resistant layer 88; cooling the corrosion resistant layer 88 to prevent the accumulation of insoluble salts on the liner 82; lowering the service temperature of the walls 15 of the vessel 12; withdrawing heat from the reactor chamber 14 for heat
30 recovery; and contracting the liner 82 to detach the liner 82 from the wall 15 during removal of the liner 82 from the vessel 12. To accomplish these functions, connectors 96 are provided that extend through the wall 15 of the

vessel 12 to the porous layer 86. Each connector 96 allows a passageway 98 to the porous layer 86 from outside the vessel 12.

With combined reference to Figures 1 and 2, it can be seen that a pump 100 can be placed in fluid communication with the porous layer 86 to thereby allow a heat transfer fluid 102 to be pumped into and through the porous layer 86. Specifically, as shown, a heat transfer fluid 102 can be pumped from reservoir 104 through line 106 to a connector 96. For use in the present invention, the heat transfer fluid 102 can be water, ethylene or propylene glycol, an inert gas or any other fluid suitable for use as a heat transfer fluid at the temperatures contemplated and described above.

Referring now to Figure 2, it can be seen that the heat transfer fluid 102 is pumped from line 106 through connector 96a via passageway 98a and into porous layer 86. After circulation within porous layer 86, heat transfer fluid 102 exits the porous layer 86 through connector 96b via passageway 98b and flows into line 108. As described below, a heat transfer fluid 102 can be pumped through the porous layer 86 for several purposes. For example, a heat transfer fluid 102 can be pumped through the porous layer 86 to pre-heat the reactor chamber 14. Referring now to Figure 1, a preheater 110 is shown positioned along line 106 to preheat heat transfer fluid 102 prior to entering the porous layer 86. Specifically, the reactor chamber 14 can be preheated during periods preceding steady state reactor conditions. As discussed above, combustion of the reactants 20 in the reactor chamber 14 produces heat, and this heat can be used to obtain and maintain the temperatures and pressures required for the hydrothermal treatment. Once the desired temperature and pressure within the reactor chamber 14 is obtained, the feed rates of the reactants 20, auxiliary fuel 24, water 38 and oxidizer 39 can be adjusted to maintain steady state reactor temperatures and pressures. Prior to obtaining the steady state reactor temperature, the chamber 14 can be preheated by passing a preheated heat transfer fluid through the porous layer 86. It is to be appreciated that for applications that do not require a preheated heat transfer fluid 102, the preheater 110 can be bypassed or turned off.

During hydrothermal treatment, a heat transfer fluid 102 can be passed through the porous layer 86 to cool the corrosion resistant layer 88 of the liner 82 and a thin layer of fluid in the reactor chamber 14 that is immediately adjacent to the liner 82. It is known that below certain temperatures (solubility inversion temperature), inorganic salts become highly soluble in water. As explained above, during normal hydrothermal treatment conditions, most inorganic salts are insoluble due to the high temperatures and pressures in the reactor chamber 14. In the absence of specific precautions, these inorganic salts are free to deposit and accumulate on exposed surfaces, often plugging the reactor vessel. By maintaining the temperature of the corrosion resistant layer 88 and a thin layer of fluid in the reactor chamber 14 that is immediately adjacent to the liner 82 below the solubility inversion temperature, solids near the corrosion resistant layer are forced to dissolve rather than deposit on the surface of the corrosion resistant layer 88. Also explained above, corrosion rates generally increase with increasing temperature. Consequently, reducing the temperature of the corrosion resistant layer 88 can effectively decrease the rate of corrosion when liner 82 is exposed to corrosives in the reaction stream 60.

Also in accordance with the present invention, during hydrothermal treatment, a heat transfer fluid 102 can be passed through the porous layer 86 to cool the pressure bearing wall 15 of the reactor vessel 12. It is to be appreciated that by lowering the service temperature of the pressure bearing wall 15, thinner wall sections and / or less exotic materials can be used in constructing the vessel 12. In an alternative embodiment shown in Figure 3, a layer of insulation 112 can be positioned between the porous layer 86 of the liner 82 and the wall 15 to lower the service temperature of the pressure bearing wall 15. In the embodiment of the present invention shown in Figure 3, a heat transfer fluid 102 can still be passed through the porous layer 86 to cool the corrosion resistant layer 88, to preheat the reactor chamber 14, or as discussed below, to recover heat from the hydrothermal treatment.

With combined reference to Figures 1 and 2, it will be seen that a heat transfer fluid 102 can also be pumped through the porous layer 86 to recover

heat generated during hydrothermal treatment. As shown in Figure 1, heat transfer fluid 102 exiting the vessel 12 through line 108 can be sent to a heat exchanger 114 for heat recovery and then routed to a reservoir 116.

Referring now to Figure 2, a partition 118 can be used to divide the porous layer into sections 120, 122, isolating section 120 from section 122. Although only one partition 118 is shown in Figure 2, it is to be appreciated that more than one partition 118 may be used in accordance with the present invention. As shown in Figure 2, separate connectors 96 can be provided for each section 120, 122, allowing for independent pumping of heat transfer fluid 102 through each section 120, 122. Specifically, heat transfer fluid 102 can be pumped from line 106 into section 120 of porous layer 86, entering through connector 96a and exiting through connector 96b. Similarly, heat transfer fluid 102 can be pumped from line 106' into section 122 of porous layer 86, entering through connector 96a' and exiting through connector 96b'. Although the additional line 106' is not shown in Figure 1, it is to be appreciated that an additional line, pump and reservoir can be provided to accommodate each additional section 120, 122.

Also in accordance with the present invention, as shown in Figure 2, each section 120, 122 of the porous layer 86 can be monitored to ensure that the high pressure reaction stream 60 is not leaking through the corrosion resistant layer 88 of the liner 82. Specifically, connectors 96, such as connector 96c shown in Figure 2, can be provided that extend through the pressure bearing wall 15 of the vessel 12 allowing access to the porous layer 86 for monitoring. Although not shown in the Figures, it is to be appreciated that a single connector 96 could function both as a passageway 98 for pumping a heat transfer fluid 102 into the porous layer 86 and to provide access for leak detection. In one embodiment of the present invention, an external sensor 124 can be positioned outside the vessel 12 as shown in Figure 2. Fluid communication between the external sensor 124 and section 120 of the porous layer 86 is provided by the connector 96c. Specifically, fluid from section 120 is allowed to flow through the passageway 98c to the external sensor 124 and preferably, back to the porous layer 86. For the

present invention, the external sensor 124 can be a device capable of measuring flow rate, pressure, pH, temperature, the presence of any chemical species known to be in the reactor chamber 14, or any other property known in the pertinent art which will indicate that a leak has developed in the corrosion resistant layer 88 of the liner 82. It is to be appreciated that each section 120, 122 can be monitored by a separate external sensor 124 (for example, Figure 2 shows section 122 being monitored by external sensor 124') or each section 120, 122 can be piped together for monitoring by a single external sensor 124.

10 In another embodiment of the present invention, as shown in Figure 3, internal sensors 126 can be provided to monitor each section 120, 122 of the porous layer 86 to ensure that the corrosion resistant layer 88 of the liner 82 is not leaking. In this embodiment, connectors 96, such as connector 96d shown in Figure 3, can be provided that extend through the pressure bearing wall 15 of the vessel 12 allowing a signal from the internal sensor 126 to be sent through the passageway 98d over wire(s) 128 to a display / recorder 130 located outside the vessel 12. It is to be appreciated that the signal from the internal sensor 126 could also be sent to a controller having a processor (not shown). For the present invention, the internal sensor 126 can be a device capable of measuring flow rate, pressure, pH, temperature, the presence of any chemical species known to be in the reactor chamber 14, or any other property known in the pertinent art which will indicate that a leak has developed in the corrosion resistant layer 88 of the liner 82. It is to be appreciated that each section 120, 122 can be monitored by a separate internal sensor 126 (for example, Figure 3 shows section 122 being monitored by external sensor 126').

Returning now to Figure 1, it will be seen that as the reaction stream 60 is removed from the vessel 12 it is passed through the line 77 to a cooler 132. As contemplated for system 10, the cooler 132 may use regenerative heat exchange with cool reactor stream, or heat exchange with ambient or pressurized air, or a separate water supply, such as from a steam generator (not shown). Once cooled by the cooler 132, the high pressure reactor

stream is then depressurized. Preferably, depressurization is accomplished using a capillary 134. It will be appreciated, however, that a pressure control valve or orifice (not shown) can be used in lieu of, or in addition to, the capillary 134.

5 After the effluent 78 from the reactor chamber 14 has been both cooled by the cooler 132 and depressurized by capillary 134, it can be sampled through the line 136. Otherwise, the effluent 78 is passed through the line 138 and into the liquid-gas separator 140. To allow accumulation of a representative sample in separator 140, it can be diverted to either tank 142
10 during startup of the system 10, or to tank 144 during the shutdown of system 10. During normal operation of the system 10, the line 146 and valve 148 can be used to draw off liquid 150 from the collected effluent. Additionally, gas 152 from the headspace of separator 140 can be withdrawn through the line 154 and sampled, if desired, from the line 156. Alternatively, the gas 152 can
15 be passed through the filter 158 and valve 160 for release as a nontoxic gas 162 into the atmosphere. As will be appreciated by the person of ordinary skill in the pertinent art, a supply tank 164 filled with an alkali agent 166 can be used and the agent 166 introduced into the separator 140 via line 168 to counteract any acids that may be present.

20 While the particular systems and methods for hydrothermal treatment as herein shown and disclosed in detail are fully capable of obtaining the objects and providing the advantages herein before stated, it is to be understood that they are merely illustrative of the presently preferred embodiments of the invention and that no limitations are intended to the
25 details of construction or design herein shown other than as described in the appended claims.